

# Cyclic olefin copolymer-silica nanocomposites foams

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Abstract A cyclic olefin copolymer (COC) matrix was melt compounded with various amounts of fumed silica nanoparticles (1, 3 and 5 vol%) and the resulting materials were foamed through supercritical carbon dioxide. Foams were produced at four different foaming pressures (90, 110, 130, and 150 bar), keeping all other processing parameters constant. The main physical properties of both bulk and foamed samples were investigated in order to assess the role of both nanofiller content and foaming pressure. It was observed that the density values of the foamed materials decreased as the foaming pressure increased and that the presence of nanofillers leads to slightly denser materials. Both scanning and transmission electron microscopy evidenced the presence of filler aggregates on the bulk composites. These aggregates resulted to be elongated along the cell wall direction upon foaming. Dynamic mechanical thermal analysis, quasi-static tensile tests, and creep tests evidenced a positive effect played by nanosilica in improving the stiffness, the strength, and the creep stability of the polymer matrix for all foaming pressures. The application of a theoretical model for closed-cell foams highlighted how the stiffening effect provided by the nanosilica networking is mostly effective at elevated filler amounts and reduced foaming pressure values.

## Introduction

Polymeric foams are utilized in a wide variety of applications, but their synthesis and manufacturing generally requires enormous quantities of organic and halogenated solvents. It was estimated that about fifteen billion kilograms of solvents are worldwide produced every year, and their application represents a critical environmental problem, because of the noticeable emission of toxic compounds and of polluted waste water production [1]. Therefore, in the last years the utilization of non-toxic solvents and of eco-friendly manufacturing processes has become a key issue. Recently, many research groups have proposed various possible alternatives, and among them the application of supercritical fluids (SCFs) seems to be the most promising and convincing way [2-11]. A fluid reaches a supercritical state at a temperature and pressure above its critical point. This stage is characterized by the inability to distinguish whether the matter is a liquid or a gas. As a result, SCFs do not possess a definite phase. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned." In fact, polymer matrix foaming with SCFs allows to avoid organic solvents and presents several advantages from a chemical, physical, and toxicological point of view. The use of SCFs is not limited to the laboratory field, but it can be successfully applied also at an industrial scale [12]. Among supercritical fluids, carbon dioxide is the most utilized, because of its easy processability, cheapness, non-toxicity, and non-flammability [13, 14].

In the last years, thermoplastic polymers synthesized through metallocene-based catalysts have attracted the attention of many researchers and producers [15].

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Particular interest has been devoted to cyclic olefin copolymers (COCs) [16, 17], which are amorphous thermoplastics obtained by copolymerization of norbornene and ethylene. COCs are characterized by remarkable properties in terms of stiffness, high chemical resistance, good moisture barrier properties, low moisture absorption, and low density. Therefore, COCs are suitable for the production of transparent moldings (optical data storage, lenses, and sensors), packaging of drugs, medical and diagnostic devices, food containers, etc. Considering that the glass transition temperature  $(T_g)$  of COCs can be tailored by varying the percentage of norbornene [18], various COC grades suitable for specific applications are available on the market. Also polyolefin/COC blends, especially polypropylene/COC blends and polyethylene/COC blends, are very interesting materials from a scientific and industrial point of view [19, 20].

Polymer matrix nanocomposites have been studied in recent years as innovative materials. In fact, the incorporation of nanofillers at low concentrations (5-10 wt%) into a polymer matrix can significantly improve its mechanical properties, its dimensional stability, its thermal degradation and chemical resistance, and also gas and solvent impermeability [21]. The typical drawbacks (i.e., embrittlement, loss of transparency, loss of lightness) associated with the use of traditional inorganic microfillers can be generally avoided [22]. Quite surprisingly, less attention has been devoted in the open literature to nanocomposite systems filled with isodimensional nanofillers, such as fumed silica nanoparticles. Fumed silica nanoparticles are industrially produced in a wide range of specific surface area (ranging from 50 to 400 m<sup>2</sup>/g) and with a variety of surface treatments from hydrophilic to hydrophobic. Due to the elevated specific surface area, this nanofiller self-aggregates when dispersed in polymer matrices, forming an interconnected network of interacting particles [23-25]. It has been recently demonstrated by our group that the mechanical properties of thermoplastic matrices can be remarkably improved by the introduction of this kind of nanoparticles [26]. A certain interest has recently arisen for polymeric nanocomposites foamed through supercritical carbon dioxide  $(scCO_2)$  [7, 8]. For instance, Chen et al. performed an experimental and theoretical investigation of the compressive properties of multi-walled carbon nanotubes (MWNTs)/poly (methyl methacrylate) nanocomposite foams [27]. They reported that the addition of MWNTs increased both the Young's modulus and the compressive properties of polymer foams. In another work of Strauss et al. [10] on scCO<sub>2</sub> processed polystyrene nanocomposite foams, it was demonstrated how the foaming process altered both the thermal and morphological features of the prepared materials. Bhattacharya et al. [2] in their work on the foaming behavior of polypropylene/clay nanocomposites studied the effect of the foaming parameters (i.e., saturation pressure and temperature, foaming temperature, foaming time, and quench temperature) on the properties and morphology of the produced materials. To the best of our knowledge, no papers on COC/silica nanocomposites foamed with scCO<sub>2</sub> can be found in the open scientific literature.

On the basis of these considerations and taking into account the increasing interest on COCs as lightweight engineering materials, the objective of the present work is to prepare and characterize COC/silica nanocomposites at various filler concentrations, to be then foamed through a supercritical carbon dioxide process. A general comparison between bulk and foamed samples will be then carried out, in order to evaluate the real effectiveness of fumed silica nanoparticles in improving the thermo-mechanical properties of the foams. Moreover, a detailed analysis of the influence of the foaming processing parameters on the physical properties of the produced materials will be presented.

# Materials and methods

#### Materials

Cyclic olefin copolymer TOPAS<sup>®</sup> 8007 (MFI at 2.16 kg, 190 °C = 2.16 g/10 min, density = 1020 g/dm<sup>3</sup>) was supplied by Ticona (Florence, Kentuky) in form of chips. Untreated fumed silica nanoparticles Aerosil<sup>®</sup> A200 (A200), having a specific surface area of 200 m<sup>2</sup>/g and a mean primary particle size of 12 nm, were provided by Evonik (Frankfurt, Germany). Both materials were utilized as received.

# Sample preparation

Bulk samples were prepared through a melt compounding process using a Thermo Haake Rheomix 600p at a temperature of 190 °C, a rotor speed of 90 rpm, and a mixing time of 15 min. The resulting materials were then hot pressed in a Carver laboratory press at the same temperature, in order to obtain square sheets of composite samples having a thickness of 0.8 mm and a width of 10 cm. In this way, neat COC matrix and nanocomposite samples with volume fractions of 1, 3, and 5 vol% were prepared.

In Fig. 1, a schematic representation of the  $scCO_2$  foaming plant is reported with the main components: the tank where  $CO_2$  is stored, the cryostat to cool down the fluid, the pump to increase the pressure of the incoming  $CO_2$  to the reactor, and a resistor to heat the reactor chamber. A Berghof High Preactor BR-300 with a capacity of 700 ml was utilized as reactor chamber. The foaming





process basically occurred in three stages:  $scCO_2$  sorption, foaming, and cell fixation. It should be noted that both the nature of the polymeric matrix and the processing parameters affect the expansion process with  $scCO_2$  and the properties of the resulting foams [28–33]. In this work, the foaming pressure was considered as the only variable parameter in the foaming process, while temperature, processing time, and depressurization rate were taken constants. In fact, in several studies it was reported how the foaming pressure is one of the most important parameters affecting the cell's morphology [3, 33, 34]. A schematic



Fig. 2 Time dependency of the processing parameters (pressure and temperature) during the foaming process

view of the processing parameters variation during the foaming process is reported in Fig. 2. Bulk samples were cut from the compression molded sheets in rectangles 2 cm long and 0.5 cm wide. Subsequently, they were inserted in the reaction chamber and the temperature was increased up to a constant value of 90 °C (i.e., 10 °C above the glass transition temperature of neat COC). This temperature was chosen in order to have a good deformability and elevated scCO<sub>2</sub> permeability of the COC matrix. It should be pointed out that a processing temperature higher than the glass transition temperature is a mandatory condition for an effective foaming. On the other hand, higher temperatures promote the diffusion of the scCO<sub>2</sub> out from the polymeric matrix [27, 35] and a reduction of the foam density [33]. Supercritical CO<sub>2</sub> was then purged in the reactor for 30 min at four different pressures (90, 110, 130, and 150 bar) to promote the  $scCO_2$  sorption. The sorption time was choosen after a long preliminary experimental activity, in order to obtain an uniform diffusion of the supercritical fluid within the polymeric matrix. A subsequent depressurization stage was then performed to obtain the foaming of the samples. The depressurization rate was set at 0.1 l/min in order to maintain a constant chamber temperature. A subsequent cooling down to room temperature at 2 °C/ min was performed in order to promote the cell fixation. In this way, both neat COC and nanocomposite foams at different nanofiller contents (1, 3, and 5 vol%) were prepared.

Bulk samples were denoted indicating the matrix, the nanofiller type and its volume concentration. For instance, COC-A200-1 denotes the nanocomposite bulk sample with

a silica content of 1 vol%. Foamed samples were designated indicating the matrix, the filler type, the filler content, and the foaming pressure. As an example, COC-A200-5\_e90 indicates the nanocomposite foam with a filler amount of 5 vol%, expanded at 90 bar.

# **Experimental methodologies**

Density measurements were carried out by using a Gibertini E42 hydrostatic balance through the Archimedes' principle. Acetone was used as testing liquid, because its density is lower than that of the water. The distribution of the cell size was measured through an Heerbrugg Wild M3Z optical microscope, and a statistical analysis was then performed to determine the mean cell diameter and the relative standard deviation values. The microstructural features of the cell walls (i.e., cell size distribution) were observed through a Carl Zeiss AG Supra 40 FESEM microscope, operating at an acceleration voltage of 1.5 kV, and at different magnifications. Before the observations, samples were cryofractured in liquid nitrogen and then metalized. At least three images at the same magnification were taken for each composition. A TEM microscope Tecnai G2 Spirit Twin FEI at an accelerating voltage of 120 kV was used to investigate the silica dispersion within the polymeric matrix of both bulk and foamed materials with bright field (BF) imaging mode. Ultrathin specimens (thickness of about 50 nm) were prepared at room temperature by using an Ultracut UCT Leica ultramicrotome.

Thermogravimetric analysis was performed both on bulk and on the foamed samples trough a Mettler TG50 thermobalance under an air flow of 150 ml/min. Samples were tested from 50 to 700 °C at an heating rate of 10 C/min. Only one specimen was tested for each composition. In this way, the decomposition temperature  $(T_d)$ , i.e., the temperature corresponding to the maximum mass loss rate, was determined.

Dynamical mechanical analysis (DMTA) was performed in tensile mode both on bulk and foamed materials using a Q800 DMA machine (TA Instruments, USA). Rectangular samples 5 mm wide and 0.8 mm thick were tested at a frequency of 1 Hz (gage length of 10 mm) in a temperature interval between 20 and 120 °C at an heating rate of 3 °C/ min. A strain amplitude equal to a deformation level of 0.05 % was applied both for the bulk and for the foamed materials. Only one specimen was tested for each composition. In this way, it was possible to determine the temperature dependence of the dynamic moduli (E' and E") and of the loss tangent (tan  $\delta$ ).

Quasi-static tensile tests were performed through an Instron 4502 tensile testing machine, equipped with a load cell of 1 kN. Bulk samples were tested using ISO 527 1BA samples, with a gage length of 30 mm. Elastic modulus

was evaluated at 1 mm/min, using a resistance extensometer having a gage length of 12.5 mm, while tensile tests at break were carried out without the extensometer at a crosshead speed of 5 mm/min. Tensile properties at break of foamed samples were evaluated at 5 mm/min using rectangular samples with a width of 5 mm and a gage length of 15 mm. The mean thickness of the foamed specimens comprised between 3.0 and 3.5 mm, depending on the foaming pressure. All tests were performed at ambient temperature, and at least five specimens were tested for each sample.

Creep tests were carried out by a Q800 DMA machine (TA Instruments, USA), setting a testing temperature of 30 °C, and a creep time of 60 min, applying a constant stress equal to the 10 % of the ultimate tensile strength of the neat matrix. Rectangular samples 5 mm wide and with a gage length of 10 mm were utilized to test both the bulk samples and the polymer foams.

# **Results and discussion**

#### Microstructural characterization

In Fig. 3a and in b, representative optical microscope images of the nanocomposite foams with a silica loading of 5 vol% prepared applying a foaming pressure of 90 and 150 bar are, respectively, shown. It can be noticed that the prepared samples are characterized by a closedcell morphology. In Fig. 4a, the density of neat COC and of the relative nanocomposites as a function of the foaming pressure is reported, while in Fig. 4b the mean cell size values are collected. It can be noticed that unfilled materials foamed at 90 bar present a density reduction of about 73 % with respect to the corresponding bulk materials, and the density drop is even more pronounced at higher foaming pressures. A systematic increase of the foam density was detected for the nanofilled samples, because of the higher density of fumed silica with respect to COC. Correspondingly, cell size slightly increases with the applied pressure, regardless of the nanofiller amount. However, considering standard deviation values associated to these measurements, it can be concluded that the variation of the cell diameter with the applied pressure is practically negligible. Also the dependency of the foam density from the nanofiller amount seems to be very weak.

In Fig. 5a a FESEM micrograph of the cryofractured section of the COC-A200-3 bulk sample is reported. The presence of silica aggregates with irregular shape uniformly dispersed within the matrix, with a mean size of around 100 nm, can be noticed. Interestingly, the presence of some voids around the nanoparticles indicates a non-



Fig. 3 Representative optical microscope images of a COC-A200-5\_e90 and b COC-A200-5\_e150 samples



Fig. 4 a Density and b mean cell size of the neat COC and relative nanocomposites as a function of the foaming pressure



Fig. 5 FESEM micrographs of a COC-A200-3 sample and b and c of cell walls of COC-A200-3\_e150 sample

perfect interfacial adhesion between the polymer matrix and silica aggregates. It is also interesting to observe the cryofractured section of the cell wall of the same nanocomposite foamed with  $scCO_2$  at 150 bar (Fig. 5b, c). An evident deformation of the aggregates in a direction parallel to the cell walls can be observed. A confirmation of this observation comes also from TEM analysis of the same samples (see Fig. 6a, b, respectively). In fact, the TEM picture of bulk nanocomposite sample reported in Fig. 6a confirms the presence of nanosilica aggregates uniformly distributed within the matrix. On the other hand, as a consequence of the foaming process a visible deformation and reorientation of these aggregates parallel to the cell walls borders can be clearly noticed (Fig. 6b). A similar phenomenon has been reported for the strain-induced deformation of nanosilica aggregates in highly drawn highdensity polyethylene fibers [36] and linear low-density polyethylene sheets [23].





#### **Thermal properties**

Thermogravimetric analysis was carried out in order to evaluate the thermal stability of both bulk and foamed materials. In Fig. 7a, mass loss curves of bulk materials are reported, while Fig. 7b shows the decomposition temperature  $T_{\rm d}$  (i.e., the temperature associated to the maximum mass loss rate) of the foamed materials. Interestingly, it can be observed how silica introduction can positively affect the thermo-oxidative stability of both bulk and foamed materials over the whole range of foaming pressures, with a systematic increase of the decomposition temperature  $(T_d)$ with the nanofiller amount. Similar results were reported for COC-based nanocomposites by this group [26] and by Ou et al. [16, 17]. From Fig. 7b it is evident than an increase of the foaming pressure leads to a decrease of the decomposition temperature  $(T_d)$ , probably because of the corresponding increase in the cell diameter and the consequent increase of the surface area exposed to thermaloxidative degradation.

Dynamical mechanical analysis was also carried out in order to evaluate the viscoelastic properties of both bulk and foamed materials. While glass transition temperature  $(T_{g})$ seems to be practically unaffected by nanofiller introduction and by the foaming process, from Fig. 8a an increase of the storage modulus with the nanofiller amount can be detected for bulk samples. In particular, an E' increment of about 31 % can be observed with a nanosilica content of 5 vol%. In Fig. 8b, the storage modulus evaluated at 20 °C ( $E'_{20}$ ) of neat COC and nanocomposite foams as a function of the foaming pressure is represented. It is interesting to note how  $E'_{20}$ decreases with the applied pressure and how nanosilica introduction leads to a noticeable increase of the storage modulus at all the applied foaming pressures. In fact a 3.6-time increment with respect to the neat matrix can be observed by adding 5 vol% of nanosilica at a foaming pressure of 90 bar.



Fig. 7 Thermogravimetric analysis of neat COC and relative nanocomposites: a mass loss curves of bulk samples and b decomposition temperature of nanocomposite samples



Fig. 8 Dynamic mechanical analysis of neat COC and relative nanocomposites. a Storage modulus curves of bulk samples and b storage modulus evaluated at 20 °C of nanocomposite foams. For

#### **(b)** 1000 – COC\_e - COC-A200-1\_e - COC-A200-3\_e 800 COC-A200-5\_e E'<sub>20</sub> (MPa) 600 400 200 0 100 120 90 110 130 140 150 foaming pressure (bar)

bulk materials the following storage moduli were obtained at 20 °C: for COC = 2135 MPa, for COC-A200-1 = 2239 MPa, for COC-A200-3 = 2544 MPa, for COC-A200-5 = 2805 MPa

# **Mechanical properties**

In Fig. 9a representative stress-strain curves for foams expanded 90 bar are reported. All the foams show a linear behavior at low strain levels. After the yield point, plastic deformation occurs till breakage of the specimens. In Fig. 9b and c, the elastic modulus (E) and ultimate tensile strength (UTS) of the nanocomposite foams at different foaming pressures are, respectively, reported. As expected, an increase of the foaming pressure leads to a decrease of both the stiffness and of the tensile strength, because of the increase of the cell size (i.e., decrease of the foam density). Within the limits of the investigated filler ratio interval, nanosilica introduction determines a systematic enhancement of the elastic modulus with the nanofiller amount over the whole range of applied foaming pressure [37], and also the tensile strength was remarkably increased. For instance, with a foaming pressure of 90 bar, the elastic modulus of 5 vol% filled nanocomposite is about 3.5 times higher than that of the unfilled foam at the same pressure. A similar enhancement can be detected for the tensile strength. The positive effect played by the nanofiller introduction on the elastic properties of polyolefins was already reported in previous articles of this group [22, 24, 38, 39], but in the present work nanofiller introduction seems to positively affect also the tensile strength of the material. In order to confirm the positive effect played by silica nanoparticles on the mechanical behavior of bulk and foamed nanocomposites, creep tests were performed. From Fig. 10a, it can be observed how the stabilizing effect due to nanofiller introduction in the bulk materials leads to an interesting decrease of the creep compliance with respect to the neat COC. This effect is even more pronounced for foamed materials. In Fig. 10b creep compliance curves of the foams expanded at 90 bar are reported, while Fig. 10c shows the creep compliance at 3600 s of the foams as a function of the foaming pressure. In accordance with the elastic modulus results, it can be observed that the creep



Fig. 9 Quasi-static tensile tests on neat COC and relative nanocomposite foams: a representative stress–strain curves for foams expanded 90 bar, b elastic modulus, and c ultimate tensile strength of neat COC and nanocomposite foams as a function of the foaming pressure



Fig. 10 a Creep compliance curves of neat COC and relative nanocomposites (bulk materials). b Creep compliance curves of neat COC and relative nanocomposites (foamed materials) expanded at

stability increases due to nanofiller introduction along the whole range of applied pressures.

# Modeling of the mechanical response in the elastic region

In order to better evaluate the influence of nanofiller addition to the elastic modulus of the prepared foams, a modelization activity was performed. The Gibson–Ashby model [40] is commonly used to predict the elastic properties of the polymer foams. In this model the polymer foams are assumed to be composed of unit cells with cell edges, cell walls, and gas inside the cells. The Gibson–Ashby model describes the relationship between the relative modulus  $(E_r = E_{foam}/E_{bulk})$  of the polymer foams and their relative density ( $\rho_r = \rho_{foam}/\rho_{bulk}$ ) as expressed in Eq. (1):

$$E_{\rm r} = \phi^2 \rho_{\rm r}^2 + (1 - \phi) \rho_{\rm r}$$
 (1)

where  $\Phi$  is the volume fraction of polymer used for constructing cell edges, and is used as a fitting parameter.

It has been reported that the Gibson-Ashby model is not always applicable since it tends to over-estimate the relative modulus of polymer foams [27]. Such discrepancy is due to the fact that the foam is assumed to be composed of lattice or rod-like structures in which cellular walls and struts are modeled as structural shell and beam elements, respectively. The aspect ratio of the walls and struts (strut length/cross section area, or wall area/wall thickness) is supposed to be large. Such assumption is no longer valid when the density of the foam is high [41]. In addition, the  $\Phi$  value is a constant that does not depend on foam density and this may not be true for real samples. Chen et al. [27] developed a closed-cell constitutive model for predicting the compressive properties of high-density closed-cell polymer foams based on the hypothesis that foams are constituted by cubic unit cells. However, to simplify the calculation the face thickness is assumed to be equal to the

90 bar, and **c** creep compliance at 3600 s of neat COC and relative nanocomposites (foamed materials) as a function of the foaming pressure

edge thickness. In Eqs. (2) and (3), the expressions developed by Chen et al. to estimate the relative modulus  $(E_r)$  of polymeric foams are reported.

$$E_{\rm r} = \left(\frac{3A_{\rm r}^2 - 2A_{\rm r}^3}{1 - (1 - A_{\rm r})^3}\right) A_{\rm r}^4 + \beta \left(1 - \frac{3A_{\rm r}^2 - 2A_{\rm r}^3}{1 - (1 - A_{\rm r})^3}\right) \frac{A_{\rm r}}{2}$$
(2)

where

$$A_{\rm r} = 1 - (1 - \rho_{\rm r})^{\frac{1}{3}} \tag{3}$$

The  $\beta$  value is used as a fitting constant while the parameter  $A_r$  is defined to be the inverse aspect ratio of cell edges, i.e., the ratio of the edge thickness over edge length. In these conditions, the  $A_r$  value is a function of the relative density  $\rho_r$ .

In Fig. 11, the relative modulus of the foamed materials plotted against the relative density is reported. It has to be remembered that lower relative density values are associated to higher foaming pressures, and vice versa. Considering that reasonable values of  $\Phi$  are between 0.6 and 0.8 [42] and that  $\Phi$  should be less than one, it can be concluded that, even hypothesizing a limiting  $\Phi$  value of 0.99, Gibson-Ashby model is not able to fit the experimental results. On the other hand, considering a fitting with the closed-cell constitutive model (see Eq. 2), it can be concluded that with an optimized  $\beta$  value of 0.18 it is possible to satisfactorily fit the experimental results, except for higher loading contents (i.e., 5 %). The stiffening effect on nanocomposite foams due to nanosilica addition at limited contents can be predicted using the theoretical models applied to traditional foams. Therefore, it seems that the stiffening effect due to nanofiller addition in the foams is proportional to the increase of the elastic modulus produced by nanosilica in the bulk materials. It can be concluded that the microstructural mechanism responsible to the increase of the elastic properties in the bulk and in the foamed materials is the same. On the other hand, at higher



Fig. 11 Relative modulus of nanocomposite foams as a function of the relative density, with theoretical predictions according to the Gibson–Ashby (Eq. 1) and the closed-cell constitutive model (Eq. 2)

nanosilica contents (5 vol%) the elastic behavior of the foams is not explainable referring to the constitutive model, especially at lower foaming pressures (i.e., higher relative density). It seems that the increase of the stiffness of the foams experienced at higher loading levels is not proportional anymore to the enhancement of the elastic modulus of the corresponding bulk material. Therefore, it can be hypothesized that the microstructural mechanism leading to the strong improvement of the elastic features of highly loaded foams is different to those of the corresponding bulk materials. Considering FESEM and TEM micrographs of COC-A200-3\_e150 sample (Figs. 5b, 6b, respectively), an evident alignment of silica aggregates along cell wall direction was detected. It is reasonable to assume that similar alignment should be present also in polymer foams at different filler contents. Therefore, nanofiller alignment itself cannot explain the strong stiffness increase experienced for 5 vol% filled foams. Considering that the strongest deviation from the theoretical predictions were detected at higher relative density values (i.e., lower foaming pressures), it can be thought that low foaming pressures promote approaching of silica aggregates and thus the filler networking, with a consequent strong increase of the mechanical properties. On the other hand, at higher foaming pressures silica networking is impeded by the progressive alignment of the aggregates. In these conditions, it is clear that the formation of this network is possible only at high loading levels. However, this is only a tentative explanation of the obtained results and further investigations should be carried out in order to have a detailed comprehension of the role played by nanosilica addition on the elastic behavior of the foams.

#### Conclusions

Cyclic olefin copolymer-fumed silica nanocomposites were prepared at different filler amounts through a melt compounding process. The resulting materials were foamed by supercritical carbon dioxide at different foaming pressures. Bulk and foamed materials were then characterized in order to understand the role of the nanofiller amount and of the foaming pressure on their physical properties. It was observed how the nanofiller introduction systematically increased both bulk and foam density, while elevated foaming pressures promoted a consistent density reduction. Microstructural analysis on the resulting foams highlighted a progressive increase of the mean cell size with the foaming pressure, accompanied by an evident deformation of the silica aggregates along the cell wall direction. Nanosilica addition is responsible of an improvement of the mechanical properties of the foams, with a progressive enhancement of both the elastic and the fracture properties with silica amount. Also the creep stability was noticeably improved by nanosilica addition. Modelization of the elastic mechanical response of the foams through traditional models highlighted how the strong stiffening experienced at higher loading levels is due to the filler networking rather than to the alignment of silica aggregates along the cell wall direction. Concluding, foaming process of COC nanocomposites through supercritical carbon dioxide could represent an effective way to obtain low-density polymeric foams characterized by higher thermo-mechanical stability with respect to the corresponding unfilled materials.

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